Transport and Deposition of Hydrocarbons in the Plasma Generator PSI-2 : Experiment and Modelling

W. Bohmeyer 1),2), D. Naujoks 1),2), G. Fussmann 1),2), A. Markin 3), A. Loarte 4), G. Federici 5)

1) Humboldt Universität zu Berlin, Institut für Physik, Lehrstuhl Plasmaphysik, Newtonstr. 15, D-12489 Berlin, Germany
2) Association Euratom-Max-Planck Institut für Plasmaphysik, Boltzmannstr.2, D-85748 Garching bei München, Germany
3) Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky pr. 31, 119991, Moscow, Russia
4) EFDA Close Support Unit Garching, Boltzmannstr.2, D-85748 Garching bei München, Germany
5) ITER International Team, Garching Working Site, Boltzmannstr.2, D-85748 Garching bei München, Germany

e-mail contact of main author: werner.bohmeyer@ipp.mpg.de

Abstract: Decomposition, transport and deposition behaviour of injected hydrocarbons have been studied in PSI-2, a stationary plasma generator. Argon, deuterium and hydrogen plasmas with different electron densities were used in these investigations. Defined amounts of CH_4 or C_2H_4 were injected into the plasmas. A temperature controlled collector positioned some cm away from the plasma edge was used to study the formation of amorphous CH-films. The film thickness could be determined by in situ measurements. The corresponding growing rates have been compared with ERO-code modelling results. A sensitive influence of electron density on hydrocarbon decomposition–and consequently on transport and film formation – is observed and confirmed by modelling.

1. Introduction

Carbon based materials are preferably used in current fusion devices and are also intended to be used in ITER. On the other hand, the production of thick amorphous hydrocarbon films cause a significant problem, particularly because of the danger of tritium accumulation in such layers. A better understanding of the basic mechanisms leading to such layers and the identification of methods to avoid them are therefore highly desired. Carefully designed experiments as well as modelling (including an assessment of the available atomic data base) are needed for this purpose. The plasma generator PSI-2 in Berlin offers good possibilities to conduct such investigations and a series of experiments dedicated to analyse decomposition, transport and deposition of hydrocarbon molecules has been performed [1,2]. As source of the hydrocarbons defined amounts of CH_4 (methane) and C_2H_4 (ethene) were blown into the stationary plasma. The thickness of deposited layers on a temperature controlled collector (outside the plasma column) was measured in situ for different plasma conditions and gases and for different collector temperatures. ERO-code modelling with three different sets of atomic data were used. Furthermore, the sticking behaviour of the generated hydrocarbons and the carbon number density of the a-C:H films are important quantities in such comparisons.
In a preceding paper [3] we reported on large differences between experiment and modelling for hydrogen and deuterium discharges: The observed layers were up to a factor of 5 thicker than predicted by modelling. This discrepancy was a great challenge to seek for possible errors in the experimental results as well as in the numerical procedures and data entering modelling. In this paper we will see that – at least for discharges in argon – the disagreement

can largely be dissolved when using recent values for the sticking coefficient of CH in the modelling and applying the adequate density of the layers for evaluation of the experiments. Furthermore, the influence of the electron density on the decomposition of the hydrocarbons, i.e. the role of mean free path lengths compared with the dimensions of the target chamber, are meanwhile better understood and are included in the discussion. These experiments have been analysed with the 3-D Monte Carlo code ERO which has been adopted to the geometry and plasma conditions of the plasma generator PSI-2.

2. Experimental set-up

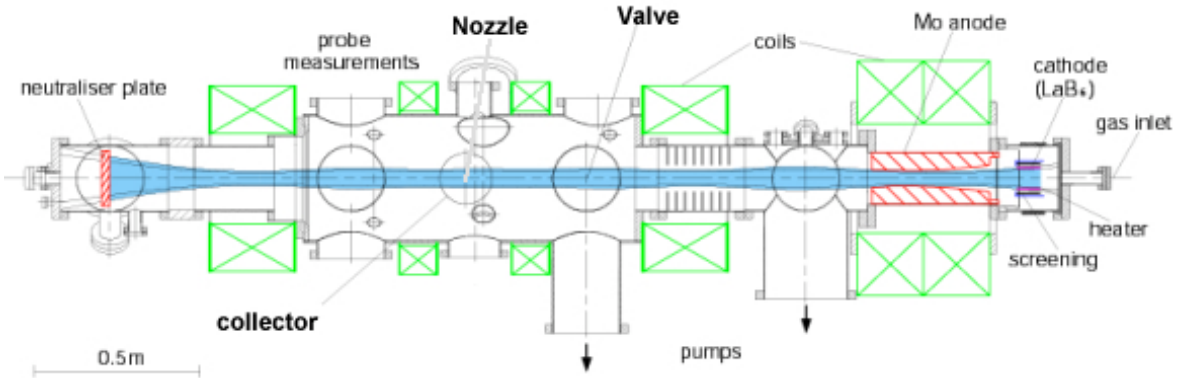

Fig. 1 Schema of the experimental set-up

The arrangement of the experiment is shown in Fig.1. A high current arc discharge between a heated LaB_6 cathode and a hollow Mo anode is the source of the plasma, which is guided by a magnetic field of B ≈ 0.1 T into the target chamber. The latter has a diameter of 0.4 m. The radial profiles of electron density and temperature are determined by Langmuir probes and these profiles are included in the modelling. For argon and hydrogen discharges the typical electron temperatures are T_e = 4 … 8 eV for discharge currents of I = 50…300 A. On the other hand, the electron density shows a more pronounced increase with current (Ar: $n_e = (2…50)\cdot10^{17}$ m^{-3}, H: $n_e = (1.5…5)\cdot10^{17}$ m^{-3}). For a recombining deuterium discharge a maximum electron density of $9\cdot10^{18}$ m^{-3} could be achieved whereas the electron temperature in this case was not larger than 1...2 eV. The diameter of the plasma column is locally varying along the axis and in the range of 6 to 8 cm. In the middle of the target chamber a floating, temperature controlled flat collector is positioned in a distance of 6 cm to the plasma edge. Furthermore, it is provided with an annular limiter (2 cm in height) that protects the collecting area from ion and electron bombardment. In fact, the floating voltage of the collector is always close to ground potential thus confirming that there is no contact with the plasma. The film thickness is determined by illuminating the Si-wafer being attached to the collector with white light and recording the reflected spectra. The optical parameters (refractive index n and extinction coefficient k) of the a-C:H films, needed to determine the film thickness, were measured by ex situ ellipsometry after the end of the experimental campaign. As indicated in Fig.1 there are two possibilities for hydrocarbon injection: 1) via a nozzle (1mm inner diameter) being located opposite to the collector and close to the plasma edge, and 2) via a valve being located on the same side but 0.40 m upstream close to the vessel wall (distance to the plasma 0.15 m).

3. Modelling

TABLE 1: HYDROCARBONS AND THEIR STICKING COEFFICIENTS USED FOR MODELLING

#	CxHy	Sticking coefficient
0	CH_4	0
1	CH_4^+	1
2	CH_3	0.001
3	CH_3^+	1
4	CH_2	0.026
5	CH_2^+	1
6	CH	0.26
7	CH^+	1
8	C	1
9	C^+	1
10	C_2H_6	0
11	$C_2H_6^+$	1
12	C_2H_5	0.01
13	C_2H_5+	1
14	C_2H_4	0
15	$C_2H_4^+$	1
16	C_2H_3	0.35
17	$C_2H_3^+$	1
18	C_2H_2	0
19	$C_2H_2^+$	1
20	C_2H	0.8
21	C_2H^+	1

The 3-D- Monte Carlo code ERO [5] was used for analysing the generation and transport of hydrocarbons. A cylinder of 0.4 m diameter (target chamber) and 0.5 m length is used as boundary volume for modelling. The flow of injected hydrocarbons through the nozzle is included in the modelling, as well as the measured electron density and temperature profiles. Most of the hydrocarbons coming from the nozzle will cross the plasma and form a beam directed to the collector plate. Depending on the plasma parameters they will be excited, ionised or dissociated, thereby producing a spectrum of C_xH_y molecules and $C_xH_y^+$ ions as well as atomic carbon and atomic and molecular hydrogen. All processes like impact ionisation by electrons, dissociation, dissociative excitation, ionisation and recombination as well as charge exchange collisions are included in the modelling. Re-erosion at the collector, however, is not included. In order to obtain good statistics one million particles are used for every run.

As a result of modelling the numbers of the various particles impinging on the collector plate are obtained in a first step. Multiplying these numbers with the specific sticking coefficients and summing over all species yields the total number of hydrocarbons forming the a-C:H film. For a given input flux of CH_4 or C_2H_4 the growth rate of the film can thus be predicted and compared with the experimental values. All species of type C_xH_y and $C_xH_y^+$ with x = 1,2 and y = 1,2,…,6 are included in the calculations. The corresponding 22 species are listed in Tab.1. The label number assigned to them will be used in Fig.7 as abscissa. In addition, the sticking coefficients for the particles as used in the calculations are given in the third column of Table 1. In contrast to our former paper [3], where CH was regarded as an essentially non-sticking molecule (s = 0.05), more recent research [4] indicated that this assumption was incorrect and we assign now a sticking coefficient of 0.26 for these particles. Furthermore, the density of the a:CH films is now taken to 1.0 g/cm^3 (see [5]) in contrast to 1.8 g/cm^3 assumed previously. This change is owed to a more careful evaluation of the optical data from which we learnt that the layers in our experiments are of soft type.

Three sets of atomic data were available and applied in the modelling: a) Erhardt and Langner [6], b) Alman, Rusic and Brooks [7] and c) Janev and Reiter [8].

For methane modelling the Janev and Reiter data package has been used, while for the case of C_2H_4 injection the Alman/Rusic/ Brooks compilation has been applied.

4. Experimental results and discussion

In addition to hydrogen and deuterium discharges, we used Ar plasmas for scanning a wide range of plasma parameters, and moreover, to avoid erosion by atomic hydrogen which is not

included in modelling. Because of the latter aspect we concentrate on Ar plasmas when comparing experiment and modelling.

The mechanism of hydrocarbon decomposition can be described as follows: For low electron density only a very small fraction of the injected hydrocarbons is immediately disintegrated to species with high sticking probability. They form a-C:H films only near to the position of injection. The non-sticking particles are reflected one or more times at the wall before entering the plasma a second time. After a number of such cycles they are eventually converted into a high sticking particle which, in general, is deposited at the wall remote from the injection position. For the same conditions a relatively large fraction of the particle input can be pumped off. The area of all pumping ports is about 8 % of the surface of the target chamber. and we may expect that the fraction of the pumped particles is of this order too. Furthermore, we expect a fairly homogeneous film formation all over the inner walls of the chamber. Or, in other words, the film formation under low electron density conditions is not a local but rather a global process: deposition is independent of the position of injection. A typical example confirming this statement is shown in Fig .2.

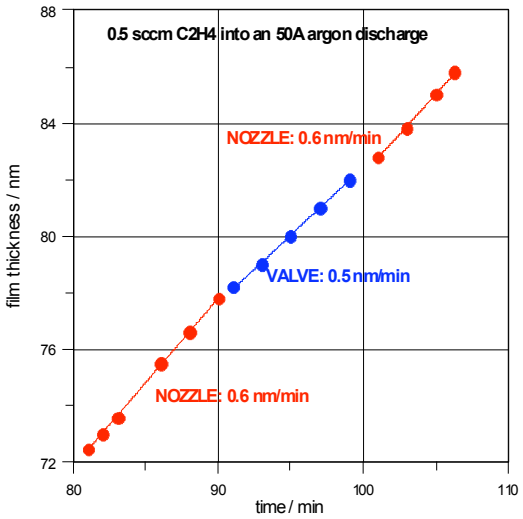

*Fig. 2: Film thickness vs. time for a low density argon discharge (n_e =2*10^{17}m^{-3}, T_e = 3 eV) with C_2H_4 injection. The growth rates are seen to be independent of the position of injection.*

Instead of simulating such a simple situation by very time-consuming modelling it is more adequate to address the problem by a rough estimation: If we inject 0.5 sccm CH_4 (1.35·10^{19} molecules per min) into the plasma and find all hydrocarbons on the wall of a cylinder of 1.2 m length (target chamber) and 0.2 m diameter (defined by the radial position of the collector) then this results in a deposition of 1.8·10^{15} C-atoms/(cm^2 min). For a soft film with a density of 1 g/cm^3 (equivalent to 5·10^{15} C-atoms /(nm*cm^2) the averaged growth rate is 0.36 nm/min. For C_2H_4 injection the growth rate is twice that large (two C-atoms per molecule), i.e. 0.72 nm/min. This result is in good agreement with Fig. 2. The experimentally determined growth rate is nearly independent of the position of injection and the rates vary between 0.48 to 0.60 nm/min, i.e. slightly smaller than estimated. A possible explanation for the remaining difference is that the lacking portion of the hydrocarbons is pumped away. From analysing the neutral gas in the target chamber by

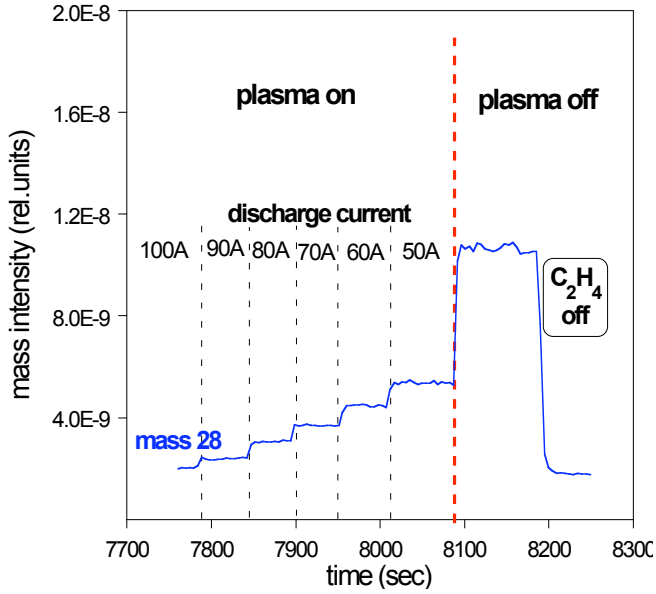

Fig. 3: Normalized mass spectrometer signal for 0.5 sccm ethylene injection(e/m=28) with and without plasma

quadrupole-mass spectrometry we know that the conversion factor – describing the degree of disintegration of the injected hydrocarbon - depends strongly on electron density.
In Fig. 3 the detected density of ethene (atomic mass number 28) is shown for the cases "with" and "without" plasma when an ethene flux of 0.5 sccm is injected into the vessel. For 100 A discharge current we detect a relatively low C_2H_4 density (about 10 % of the value without plasma). Thereafter the discharge current is ramped down and we notice an increase in ethene density with decreasing current (decreasing electron density, see Sec.2): When switching off the discharge, a further increase by a factor of 2.5 is to be noticed.

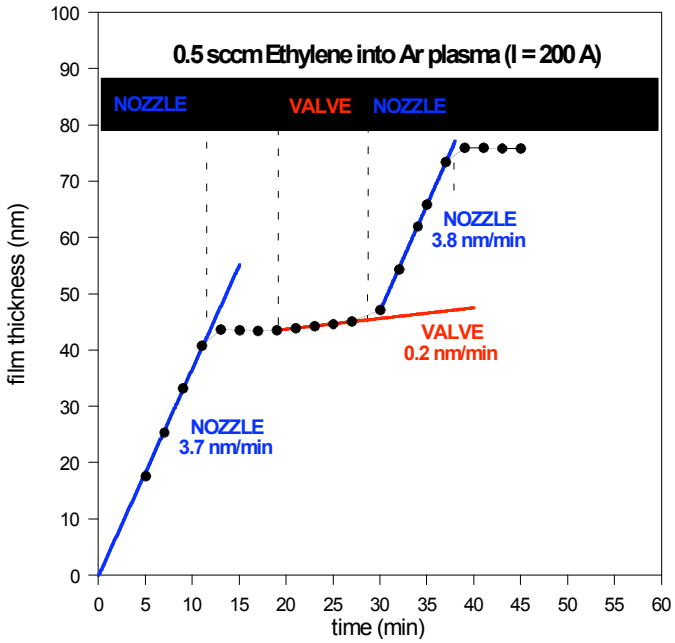

Fig. 4: Film thickness as a function of time for "nozzle" and "valve" injection into an argon discharge ($n_e = 4.5*10^{18}m^{-3}$, T_e = 5 eV)

The reduction of C_2H_4 with increasing electron density reflects the conversion to non sticking species forming films on the walls and their loss by pumping. Assuming a constant pumping rate, the results indicate that the decomposition and conversion to high sticking particles is strongly increasing with electron density. However, for a quantitative determination of the conversion factor, we would need in addition the composition of the gas that has been pumped off. Such measurements are under preparation.
For higher electron densities ($n_e > 10^{18}m^3$) we expect a more local decomposition. Most of the injected hydrocarbons will be decomposed to high sticking particles during the first passage through the plasma. For such conditions the film growing rate depends strongly on the position of hydrocarbon injection. An example is given in Fig.4. showing a great difference in film growth rates for "nozzle" and "valve" injection (see Fig.1). We found for nozzle injection a growth rate of 3.7 nm/min whereas for valve injection only 0.2 nm/min (factor 1/18) are observed. Such typical local deposition can

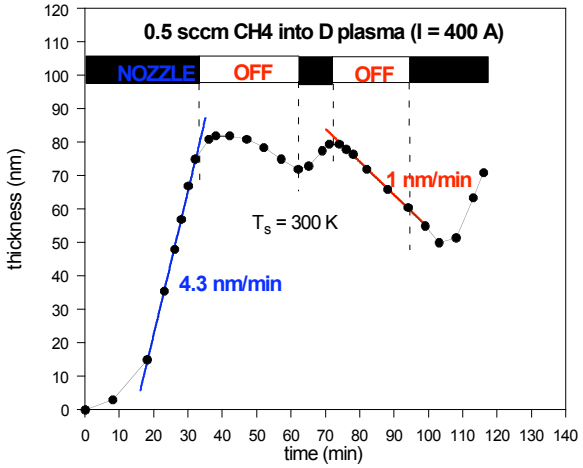

Fig. 5: Film thickness vs. time (D- plasma $n_e = 9*10^{18}m^{-3}$, T_e=2eV)

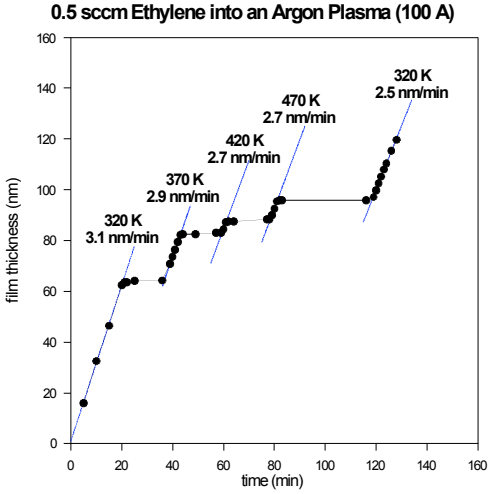

Fig 6:Film thickness vs. time for different collector temperatures ($n_e=10^{19}m^{-3}$,T_e =2 eV)

be described very well by ERO modelling. For these conditions the mean free path length for the decomposition process is comparable or smaller than the characteristic dimensions used in the modelling
In hydrogen discharges the situation is more complicated due to the erosion of the a:CH films by atomic hydrogen. This erosion mechanism is not included in the modelling since some important parameters, such as the flux density and energy of the hydrogen atoms, are very uncertain. Nevertheless, the net deposition can be determined from the experiments documented in Fig. 5 by comparing the growth rates with hydrocarbon injection ((4.3 + 1) nm/min) and without in injection (-1 nm/min).
Furthermore, the influence of the collector temperature on the deposition rate was studied. It is found that the rates are nearly independent of temperature (up to 470 K) in case of argon (see Fig.6), whereas in hydrogen the growth mechanism is influenced by (a temperature dependent) erosion process [2].

5. Comparison between modelling and experiment

In the left part of Fig. 7 a " D density plot of the hydrocarbons sticking on the collector as obtained by modelling is shown. Also the profiles across the collector in the x- and y-directions are indicated. Obviously a rather homogeneous deposition is predicted. In the right hand part of the same figure the fractions of impinging and sticking particles are plotted as a function of the species label given in Table 1. These graphs demonstrate that a wide spectrum of hydrocarbons is produced in the plasma and that can hit the collector. However only four species (#6: CH, #8: C, #16: C_2H_3, #20: C_2H) out of these do contribute to film formation. Quantitatively, for the injected flux of CH_4 an integral film growth of 1.9 nm/min is predicted. This value has to be compared with 3.7 nm/min found in the experiment (Fig.4).

For studying the deposition efficiency as a function of electron density the measured radial n_e-profile of a 200 A discharge (n_e = (4...5) $\cdot 10^{18}$ m^{-3}) in argon was taken and scaled with a factor. The results, depicted in Fig. 8., show the maximum deposition rate on the collector in dependence on the central electron density. Three experimental points are included in the figure. In qualitative agreement with modelling they show a strong increase of the growth rate with electron density in the low density range. Modelling, however, predicts in addition a maximum growth rate (see insert in Fig. 8) of 2.2 nm/min for $n_e = 10^{19}$ m^{-3} which – so far – could not be confirmed in the experiments. Higher density experiments are therefore to be striven for. Physically, the predicted maximum results from a decrease of the probability that the decomposed particles can reach the collector with rising density. At high densities the decomposition takes place close to location where the particles are injected. Thereby the distance between collector and the region where the particles with high sticking probability are produced is increasing. In addition the probability of loosing charged species along the magnetic field line is also enhanced. In the simulation the deposition rate decreases for electron densities greater than 10^{19} m^{-3}. More specifically, it was found that the flux of such high sticking species as C_2H toward the collector is decreasing with increasing density while the amount of impinging carbon atoms remains nearly constant. In general, only a small part of the injected carbon atoms (about 2 - 4 %) is found deposited on the collector. Therefore, the deposition is controlled by a very sensitive interplay of the multitude of reactions in the plasma and the sticking behaviour at the surface.

The differences between experiment and modelling to be seen in Fig. 8 are within the range of the expected errors. Nevertheless, there are also some fundamental sources of errors

conceivable. For example, the atomic data refer to the case that all molecules are in the ground state which might not be true in reality where the particles have passed the hot plasma.

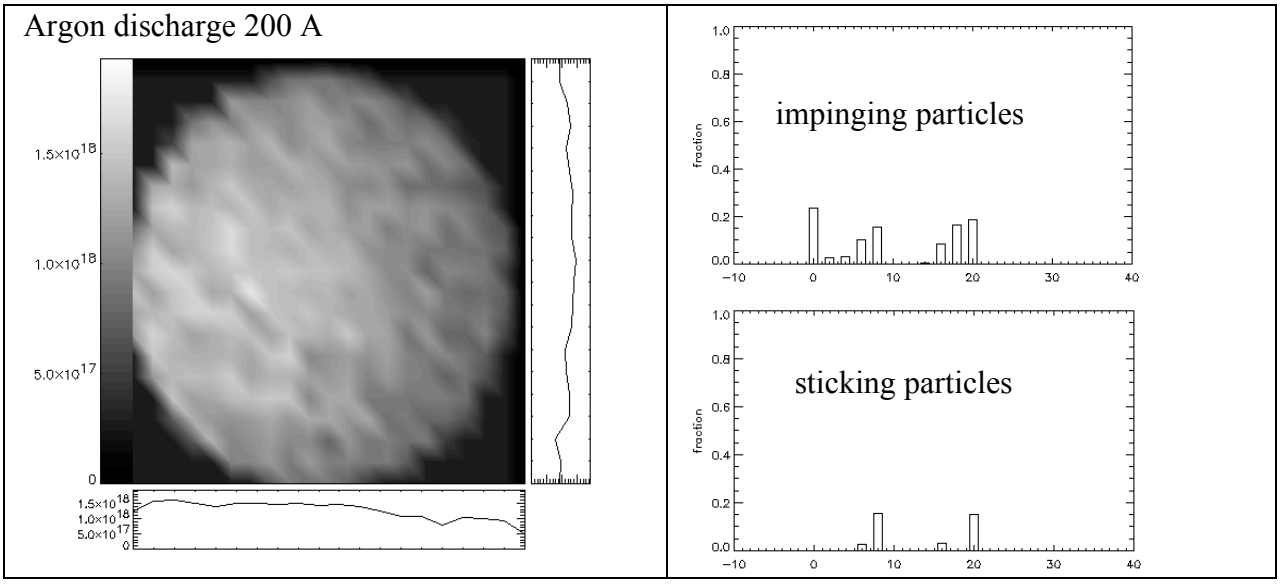

Fig.7: Flux of impinging and sticking particles modelled by ERO for a 200 A discharge in argon.

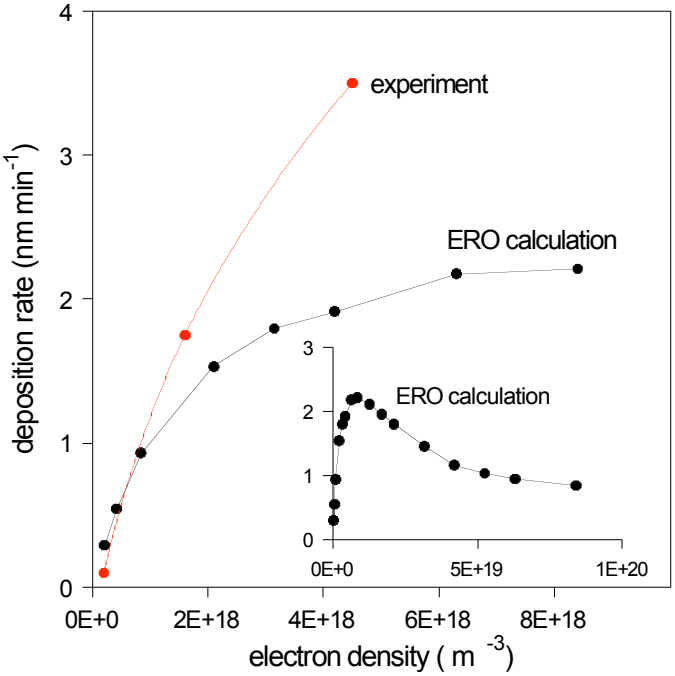

Fig. 8: Deposition rate vs. electron density according to ERO calculation. Some experimental data are included for comparison.

6. Summary

There is a pronounced difference in the deposition behaviour in hydrogen and argon plasmas. Whereas in argon practical no re-erosion is observed it is found in hydrogen plasmas and seen to increase with plasma density. In this paper the processes taking place in argon plasmas were modelled in detail using the ERO code. Using a sticking coefficient of 0.26 for CH molecules and assuming an atomic density of 1.0 g/cm3 (soft a-C:H films) the discrepancies found in a previous study are nearly dissolved and the differences between experiment and modelling are now less than a factor two. The modelling results are thus in a fair agreement with the experiments although modelling is becoming difficult and uncertain for the very low density range. For this particular regime a simple estimation of film growth rates is also in good agreement with the experimental results. Some of the remaining differences may be due to uncertainties in the atomic data base.

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7. References

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